METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF DISSOLVED ORGANIC CARBON BY UV-PROMOTED PERSULFATE OXIDATION AND INFRARED SPECTROMETRY

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U.S. GEOLOGICAL SURVEY

Open-File Report 92-480

Denver, Colorado
1993

U.S. DEPARTMENT OF THE INTERIOR

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	*by*	*To obtain*
gram (g)	3.53×10^{-2}	ounce, avoirdupois
liter (L)	2.64×10^{-1}	gallon
milligram (mg)	2.20×10^{-6}	pound
milliliter (mL)	2.64×10^{-4}	gallon

Temperature can be converted from degree Celsius (°C) to degree Fahrenheit (°F) by using the following equation:

$$^{o}F = 9/5(^{o}C) + 32.$$

Other terms and abbreviations used in this report are as follows:

ASTM	……...	American Society for Testing and Materials
DOC	……...	dissolved organic carbon
mg/L	……..	milligram per liter
OI	……..	Oceanographic International1
sp gr	…….	specific gravity
UV	……..	ultraviolet light
v/v	……..	volume to volume

‘Use of the firm, brand, and trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey

METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY--DETERMINATION OF DISSOLVED ORGANIC CARBON BY UV-PROMOTED PERSULFATE OXIDATION AND INFRARED SPECTROMETRY

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ABSTRACT

Water samples can be analyzed for dissolved organic carbon by either an Oceanographic International (OI) carbon analyzer or a Dohrmann carbon analyzer. Thirty natural-water samples were analyzed by both techniques, and then precision between the two techniques was evaluated. Linear regression analysis was used to evaluate bias and correlation. A paired difference test using the t statistic was used to evaluate the significance of any bias.

Distilled-water spike samples were prepared by dissolving a known amount of sodium benzoate in an exact volume of distilled water. Nine samples were analyzed by both techniques. Again, the precision between the two techniques was compared, and analyte recovery was evaluated.

The results from the spike-sample analyses of distilled water showed that the analyte recovery averaged 103 percent for the OI technique and 100 percent for the Dohrmann technique. The average absolute difference between both sets of results was ±1.8 percent from the mean of both datasets.

The linear regression analysis of data from the analysis of the natural-water samples indicated that there may be a slight bias between the two techniques. The correlation coefficient for the analysis was 0.99. The paired-difference test showed that the results of the two techniques are comparable at the 99-percent confidence level. The average absolute difference between the datasets was ±8.4 percent from the mean. The analysis indicates that the two techniques are equivalent within the realm of experimental error.

INTRODUCTION

Historically the National Water Quality Laboratory has analyzed samples for dissolved organic carbon (DOC) using the Oceanographic International (OI) model 524 carbon analyzer. This analysis also can be completed using a Dohrmann model 180 carbon analyzer. The OI and the Dohrmann carbon analyzers use a wet oxidation technique to oxidize organic carbon to carbon dioxide. OI uses heat to drive the persulfate oxidation, while the Dohrmann technique uses ultraviolet light to promote the reaction. Both instruments use nondispersive infrared spectrometry to measure the carbon dioxide produced from the oxidized carbon.

About 30 natural-water samples were analyzed using both the Dohrmann and the OI techniques. Precision between the two techniques was evaluated. Linear regression analysis was used to evaluate bias and correlation. A paired-difference test was used to evaluate the significance of any bias.

A DOC spike solution was prepared by drying sodium benzoate at *105°C* for 1 hour and cooling in a desiccator. About 0.343 g was weighed to the nearest 0.1 mg. The sodium benzoate was quantitatively transferred to a 100-mL flask and made to volume with American Society for Testing and Materials (ASTM) (1989) Type II reagent water (low carbon content). Then 25 mL of this stock solution was diluted to 500 mL; and 100 mL was rediluted to 2 L producing a carbon content of about *5* mgIL. For purposes of this method, distilled-water spikes, analyzed by both techniques on the same day, were selected for comparative evaluation. The evaluation included precision between the two techniques and analyte recovery for both.

This report describes a method for determining dissolved organic carbon which was developed by the U.S. Geological Survey for use in the Survey's National Water Quality Laboratory. The method was used to compare the results produced by both the OI and the Dohrmann carbon analyzers. The method supplements other methods of the U.S. Geological Survey for determination of organic substances in water that are discussed by Wershaw and others (1987). The method was implemented in the National Water Quality Laboratory in 1986.

This report provides a detailed description of all aspects of the method from sampling protocol through calculation and reporting of results. Precision and accuracy data are presented.

ANALYTICAL METHOD

Carbon, Organic, Dissolved by UV Catalyzed Persulfate Oxidation
and Infrared (IR) Spectrometry
Parameter Code (00681)
Method Code 0-1122-92

1. Application

This method is suitable for the analysis of water, brines, and waste water containing at least 0.1 mg/L of dissolved organic carbon (DOC). Samples containing more than 20 mg/L DOC either need to be diluted or have the sample volume reduced. The method is not suitable for the determination of volatile organic constituents.

2. Summary of Method

The sample is acidified, purged to remove carbonates and bicarbonates, and the organic carbon is oxidized to carbon dioxide with persulfate, in the presence of an ultraviolet light. The carbon dioxide is measured by nondispersive infrared spectrometry.

3. Interferences

3.1 Carbonates and bicarbonates usually present in most water are readily converted to carbon dioxide when acidified. Samples must be purged with nitrogen gas to remove carbon dioxide after acidification. Volatile organic compounds are lost during this step.

3.2 Water samples containing large concentrations of chloride ion will interfere by decomposing the persulfate oxidant and reducing UV excitation energy. This interference becomes significant when chloride concentrations are equal to or greater than 0.1 percent (1,000 mg/L).

3.3 The American Public Health Association (1989) reports that strongly acidic solutions and some brines interfere with this technique by producing infrared-absorbing aerosols.

4. Instrumentation

4.1 *Carbon Analyzer,* Dohrmann DC-80, DC-180, or equivalent, with a direct concentration read-out.

4.2 *Autosampler,* Dohrmann ASM-1, DC-180 autosampler, or equivalent.

4.3 *Microliter Syringe,* 1,000 µL**,** Unimetrics variable syringe, or equivalent

5. Apparatus

5.1 *Pipets,* TD, class A, 1, *5,* 10, 15, 20, 50, and 200 mL.

5.2 *Volumetric flask,* class A, 100, 200, and 1,000 mL.

5.3 *Autosampler vials,* 50 mL, Teflon septum screw cap.

6. Reagents

Organic carbon free water is required. ASTM Type II reagent water is suitable for the preparation of reagents. Any reagent water that yields a blank value of greater than 0.2 mg/L (DOC) should be rejected.

6.1 *Potassium persulfate,* Baker analyzed, reagent grade, granular, or equivalent.

6.2 *UV reactor reagent:* Dissolve 20 g of reagent grade potassium persulfate ($K_2S_2O_8$) in 1 L of reagent water. Add 2 mL of concentrated phosphoric acid and mix well. The pH should be 3 ± 0.2. Store in a cool dark location. The shelf life is about 1 month.

6.3 *Phosphoric acid,* concentrated (sp gr 1.69), reagent grade.

6.4 *Phosphoric acid solution (1* + 4) (inorganic carbon purge solution): Dilute 20 mL of concentrated phosphoric acid to 100 mL with reagent water.

7. Standard materials

Organic carbon free water is required for the preparation of standard solutions. ASTM Type II reagent water is suitable for this purpose.

7.1 *Carbon stock standard solution (1.00 mL = 1.0 mg C).* Dry primary standard grade potassium hydrogen phthalate at 105°C in a drying oven for 1 hour. Remove from the oven and place in a desiccator for 1 hour. Weigh 2.127 g and quantitatively transfer to a 1,000-mL volumetric flask. Dissolve the reagent, bring to volume with reagent water, and mix thoroughly.

7.2 *Carbon working solutions.* Prepare the working solutions by making the following dilutions:

1.0-mg/L solution--Pipet 1.0 mL of the stock standard solution into a 1,000-mL volumetric flask, and bring to volume with reagent water. Stopper and mix well.

5.0-mgIL solution--pipet 5.0 mL of the stock standard solution into a 1,000-mL volumetric flask, and bring to volume with reagent water. Stopper and mix well.

10.0 -mgIL solution--Pi pet 10.0 mL of the stock standard solution into a 1 ,000-mL volumetric flask, and bring to volume with reagent water. Stopper and mix well.

20.0 -mgIL solution-- Pi pet 20.0 mL of the stock standard solution into a 1,000-mL volumetric flask, and bring to volume with reagent water. Stopper and mix well.

7.3 *Sodium benzoate fortified reagent water (1.00 mL = 0.005 mg C).* Dry reagent grade sodium benzoate at 105°C for 1 hour and cool in a desiccator for 1 hour. Weigh 0.343 g and quantitatively transfer to a 200-mL volumetric flask. Bring to volume with reagent water, stopper, and mix well. Pipet 50 mL of this solution into a 1,000-mL volumetric flask, bring to volume with reagent water, stopper, and mix well. Pipet 200 mL of this solution into a 2-L volumetric flask, bring to volume with reagent water, stopper, and mix well. Use only class A pipets and volumetric flasks. This is the fortified reagent water, and the concentration is 5.0 mg/L organic carbon.

8. Sample preparation

There is no sample preparation for samples containing less than 20 mg/L DOC. The sample is injected directly into the analyzer. For samples containing more than 20 mg/L DOC, make appropriate dilutions so that the expected DOC content is between 1 and 20 mg/L.

9. Calibration

9.1 Withdraw a sample of UV reactor reagent from the UV reactor. Analyze this sample for organic carbon. Use this analysis to “zero” the instrument. Calibrate the instrument on the 10-mg/L carbon working solution, according to manufacturer’s instructions (Rosemount-Dohrmann, 1990), by injecting 1 mL of working solution into the instrument. Dohrmann carbon analyzers use single-point calibration for specific concentration ranges. Because the relation between detected area count and carbon concentration is curvilinear, these analyzers contain a linearizing circuit that compensates for this curvilinear relation.

9.2 Check calibration daily and follow manufacturer’s instructions. Standard solutions ranging from 1.0 to 20 mg/L carbon must be analyzed to confirm the accuracy of the procedure each day of operation. The analyzed value of the standard solution must be within ±10 percent of the calculated value.

9.3 Determine reagent blank by analyzing freshly drawn UV reactor reagent from the UV reactor of the reaction module. If the reagent blank is greater than 0.2 mg/L carbon, replace the reactor reagent.

9.4 Analyze a reagent-water sample fortified with a known quantity of sodium benzoate after every 20 samples to ensure the accuracy of the standards and that the instrument calibration remains constant during the analytical sample run. The analyzed value must be within ±10 percent of the calculated value.

10. Sample analysis

10.1 When using the autosampler, set analysis mode and sequence times according to the manufacturer’s instructions. Set the sample injection volume at 1 mL. If manual injection is used, inject 1 mL of sample into the external injection port and press the analyze button.

10.2 Peak integration and conversion to concentration values are performed automatically by a microprocessor in the analyzer. Analyzed values of samples are shown on the instrument display screen and are reported in milligrams of carbon per liter.

10.3 If the sample contains more than 20 mg/L DOC, either reduce the injection volume and re-inject manually or make a volumetric dilution so that the expected instrument reading is between 1 and 20 mg/L DOC. Do not reduce the injection volume to less than 0.1 mL. Dilute samples requiring injection volumes of less than 0.1 mL and re-analyze using a 1-mL injection volume.

11. Calculations

11.1 If sample dilution is required, calculate the dilution factor (DF) from the following formula:

$$DF = FV/SV$$

where FV = final volume of the dilution, in milliliters; and
SV = sample volume diluted, in milliliters.

11.2 If the sample was diluted, calculate the correction factor used to compensate for organic carbon in the dilution water from the following formula:

$$C = (VDIL \times CDIL)/FV$$

where VDIL = volume of dilution water, in milliliters;
CDIL = concentration of organic carbon in dilution water, in milligrams per liter; and
FV = final volume of diluted sample, in milliliters.

11.3 Calculate the DOC concentration in the sample with the following formula:

$$DOC, mg/L = (IR - C)(1/IV)(DF)$$

where IR = instrument reading, in milligrams per liter;
C = dilution water correction factor (zero if no dilution was used);
N = injection volume, in milliliters; and
DF = dilution factor.

12. Reporting of results

Report DOC concentration as follows: less than 10 mg/L, one decimal; 10 mg/L and greater, two significant figures.

13. Precision

Spike samples were prepared by dissolving potassium biphthalate in laboratory distilled water at four different concentrations. The concentrations were 1.0, 5.0, 15.0, and 20.0 mg/L of organic carbon. Ten replicates of each concentration were analyzed. Single operator precision and recovery information are shown in table 1.

Five samples from district sites, ranging in DOC content from about 0.3 to about 18 mg/L, were analyzed seven times each to evaluate analytical precision when analyzing natural-water samples. The results are shown in table 2.

Table *1.--Single operator precision*

[mg/L, milligrams per liter]

Theoretical organic carbon concentration of replicates (mg/L)	Number of replicates	Recovery (percent)	Mean (mg/L)	Standard deviation	Relative standard deviation (percent)
1.0	10	100	1.0	0.07	7.0
5.0	10	100	5.0	.11	2.2
15.0	10	99.3	14.9	.18	1.2
20.0	10	98.8	19.8	.16	.8

Table *2.--Method precision for natural-water samples*

[mg/L, milligrams per liter]

Number of replicates	Mean (mg/L)	Standard deviation (mg/L)	Relative standard deviation (percent)
7	0.3	0.03	8.4
7	2.3	.11	5.0
7	8.1	.34	4.2
7	13.7	.46	3.3
7	17.9	.23	1.3

DISCUSSION OF RESULTS

Spiked Distilled Water

The theoretical value of the spike solution was 5.2 mg/L (table 3). The mean analysis of the OI method was 5.4 mg/L with a standard deviation of 0.24. The mean analysis for the Dohrmann technique was 5.2 mg/L with a standard deviation of 0.14.

The recovery for the OI method averaged 103 percent and ranged from 96 to 106 percent. For the Dohrmann method, the recovery ranged from 98 to 104 percent, and the mean was 100 percent.

Table 3.--Dissolved organic carbon analysis of spiked-water samples showing results from *two carbon analyzers*

[mg/L, milligrams per liter; OI, Oceanographic International]

Sample date	Spiked amount (mg/L)	OI analysis (mg/L)	Dohrmann analysis (mg/L)	Precision[1] (percent, plus or minus)	OI recovery (percent)	Dohrmann recovery (percent)
5/17/90	5.2	5.4	5.2	1.89	103.85	100.00
5/23/90	5.2	5.8	5.4	3.57	111.54	103.85
5/29/90	5.2	5.2	5.1	.97	100.00	98.08
5/30/90	5.2	5.2	5.1	.97	100.00	98.08
6/12/90	5.2	5.4	5.3	.93	103.85	101.92
6/29/90	5.2	5.4	5.4	0	103.85	103.85
7/10/90	5.2	5.0	5.2	1.96	96.15	100.00
7/13/90	5.2	5.3	5.1	1.92	101.92	98.08
7/16/90	5.2	5.5	5.1	3.77	105.77	98.08
Mean		5.4	5.2	1.78	102.99	100.21
Standard deviation		.22	.13	1.25	4.31	2.44

[1]Precision = (absolute value a-b/2)/(a+b/2) x 100
where a = Dohrmann analysis, and
b = OI analysis.

Precision between the two techniques was evaluated by taking the absolute difference between each pair of Dohrmann and OI results, dividing the difference by 2, and expressing the result as a percentage of the mean between the Dohrmann and the OI results. The results are expressed as “percent, plus or minus.” The absolute value was used so that when the average of the dataset was taken, the positive and negative values would not cancel each other. The mean precision of the nine observations was about ±1.8 percent with a standard deviation of about 1.3. Assuming the mean between the Dohrmann and the 0! values to be the most probable value for the samples, on the average the results produced by the two techniques can be expected to agree within about ±1.8 percent of the mean when analyzing spiked distilled-water samples.

Natural-Water Matrices

The 30 natural-water samples produced a dataset which ranged from <0.1 to 6.3 mg/L. The mean for both the OI portion of the dataset and the Dohrmann portion was about 1.6 mg/L, indicating that the majority of the values was in the lower half of the range. The dataset included two Dohrmann values that were <0.1 mg/L, the reporting limit. These two values were arbitrarily set at 0.05 mg/L so that the data could be mathematically processed.

The mean precision for all samples was ±11.8 percent and ranged from 0 to 60 percent (table 4). Statistical review of the data indicated that two values were greater than three standard deviations from the mean. These values are the ones that are at or less than the reporting limit. When these two outliers are removed from the dataset, the mean improves to ±8.4 percent, with a range from 0 to 33 percent (table 5).

A linear regression analysis was used to evaluate any bias between the two techniques and to determine the degree of correlation. The correlation coefficient was 0.991. The formula for the regression line is:

$$y = - 0.22106 + 1.123x$$

Where y = Dohrmann value, and

x = OI value.

This formula suggests that a slight bias exists.

A paired-difference test using the t statistic was performed to determine if there was any statistically significant difference between the results produced by the two techniques. This test showed that the results produced by the two techniques are comparable at the 99-percent confidence level, and the apparent bias might be artificial (table 6).

CONCLUSION

The results produced by both techniques are equivalent within the realm of experimental error, and the two techniques are considered equivalent for DOC analysis.

QUALITY ASSURANCE

The following quality assurance practices are invoked during the analysis:

1. The pH of the UV reactor reagent is measured to ensure that it is in the range of 3 ±0.2.
2. The instrument is standardized with a 10.0 mg/L standard solution. Standard solutions containing 1.0, 5.0, and 20.0 mg/L organic carbon are analyzed each day to confirm the accuracy of the procedure. The analyzed value must be within ±10 or ±0.2 mg/L, whichever is larger, of the calculated value.
3. A fortified-reagent water sample of known concentration is analyzed with every 20 samples or less. The analyzed value of the sample must be within ±10 percent of the calculated value.

Table 4.--Dissolved organic carbon analysis of natural-water samples showing results from two carbon analyzers

OI, Oceanographic International; mg/L, milligrams per liter]

Sample number	OI analysis (mg/L)	Dohrmann analysis[1] (mg/L)	Precision[2] (percent, plus or minus)	Difference between OI and Dohrmann (mg/L)
901030042	2.3	2.3	0	0
901030043	2.2	2.4	4.35	-.2
901030266	1.6	1.2	14.29	.4
901090069	1	.9	5.26	. 1
901090070	.9	.8	5.88	.1
901130023	.5	.7	16.67	-.2
901130181	3.3	3.8	7.04	-.5
901150139	.6	.3	33.33	.3
901170106	1.8	1.5	9.09	.3
901170107	.8	.6	14.29	.2
901170109	1.5	1.1	15.38	.4
901170169	.3	.2	20.00	.1
901200172	.2	.05	60.00	.1
901210139	2.2	2.1	2.33	.1
901220051	1.2	1.1	4.35	.1
901220088	1.3	1.3	0	0
901220089	1.5	1.6	3.23	-.1
901220182	.8	.7	6.67	.1
901220184	.7	.5	16.67	.2
901220185	1.6	1.5	3.23	.1
901220186	5.8	6.3	4.13	-.5
901230056	2.7	2.7	0	0
901240050	1.4	1.5	3.45	-.1
901240055	4.6	4.9	3.16	-.3
901240057	.9	.6	20.00	.3
901240059	1	.9	5.26	.1
901240061	1.7	1.9	5.56	-.2
901240064	1.7	2	8.11	-.3
901240065	1.8	1.9	2.70	-.1
901240071	.2	.05	60.00	.1
Mean	1.60	1.58	11.81	.02
Standard deviation			15.08	.24

[1]Two Dohrmann values were less than the reporting limit of 0.1 mg/L. The values were arbitrarily set at 0.05 mg/L to enable mathematical processing.

[2]Precision = (absolute value a-b/2)/(a+b/2)x 100
where a = Dohrmann analysis, and
b = OI analysis.

Table 5.--Edited dataset of dissolved organic carbon analysis of natural-water samples showing *results from two carbon analyzers*

[OI, Oceanographic International; mg/L, milligrams per liter]

Sample number	OI analysis (mg/L)	Dohrmann analysis[1] (mg/L)	Precision[2] (percent, plus or minus)	Difference between OI and Dohrmann (mg/L)
901030042	2.3	2.3	0	0
901030043	2.2	2.4	4.35	-.2
901030266	1.6	1.2	14.29	.4
901090069	1	.9	5.26	.1
901090070	.9	.8	5.88	.1
901130023	.5	.7	16.67	-.2
901130181	3.3	3.8	7.04	-.5
901150139	.6	.3	33.33	.3
901170106	1.8	1.5	9.09	.3
901170107	.8	.6	14.29	.2
901170109	1.5	1.1	15.38	.4
901170169	.3	.2	20.00	.1
901210139	2.2	2.1	2.33	.1
901220051	1.2	1.1	4.35	.1
901220088	1.3	1.3	0	0
901220089	1.5	1.6	3.23	-.1
901220182	.8	.7	6.67	.1
901220184	.7	.5	16.67	.2
901220185	1.6	1.5	3.23	.1
901220186	5.8	6.3	4.13	-.5
901230056	2.7	2.7	0	0
901240050	1.4	1.5	3.45	-.1
901240055	4.6	4.9	3.16	-.3
901240057	.9	.6	20.00	.3
901240059	1	.9	5.26	.1
901240061	1.7	1.9	5.56	-.2
901240064	1.7	2	8.11	- .3
901240065	1.8	1.9	2.70	-.1
Mean	1.70	1.69	8.37	.01
Standard deviation			7.75	.24
Number of observations				28

[1]0utliers were removed from the dataset.

[2]Precision = (absolute value a-b/2)/(a-i-b/2)x 100

where a = Dohrmann analysis, and
b = OI analysis.

Table 6.--*Paired difference test of the dissolved organic carbon analysis--Dohrmann analytical technique in relation to Oceanographic International technique*

[, not equal to; <,less than; >, greater than]

Alternate hypothesis, Ha
The difference between the two methods is zero:

$$Ha: \mu o = 0$$

where μo = the mean of the differences.

Null hypothesis, Ho
The difference between the two methods is not zero:

$$Ho: \mu o\_0$$

where μo = the mean of the differences.

$$\text{Test statistic} = T = (\overline{X}diff - 0)/(Sdiff / \sqrt{ndiff})$$

where $\overline{X}diff$ = sample mean of differences,
Sdiff = sample standard deviation of differences, and
ndiff = number of differences.

Rejection region at the 99-percent confidence level

$$t < -t_{0.005} \text{ or } t > t_{0.005}$$

t @ n-1 df (30-1) and X = 0.01 is 2.76

$$T = (0.02 - 0)/(0.24 / \sqrt{30}) = 0.02 / 0.0438 = 0.46$$

In conclusion, 0.46> -2.76 and 0.46 < 2.76; therefore, T is in the acceptance range. Reject the null hypothesis at the 99-percent confidence level.

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*U.S. GOVERNMENT PRINTING OFFICE: L993-774-207/60025